Absorption Spectra of Co-ordination Compounds. IV. Ethylenediamine Cobaltic Complexes.

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Introduction. I. On Absorption Bands: In the previous papers,[1][2][3] one of the authors discussed on the origins of the selective absorption bands, which complex salts show in the near infra-red, the visible and the near ultra-violet regions of the spectrum, concluding as follows:

(a) The first absorption band: This may be attributed to electron transitions in an unsaturated transition shell of the central ion. Accordingly, if the central ion belongs to a group of typical elements, this band does not appear, because such an ion has no unsaturated transition shell. Again we should not expect this band, when the central ion, even if this belongs to a group of transition elements, has an electronic configuration of the pseudo-inert-gas or inert-gas type. An example for the former case is potassium mercuric iodide, $K_2[HgI_4]$[4], and one for the latter potassium chromate, $K_2[CrO_4]$[3].

The first absorption bands are found almost always in the visible region. Luther and others[5] discussed on the relation between the stability and the colour of complex salts. We can not determine, however, the stability of complex salt by its colour or by the position of its first absorption band, the band owing its origin to electrons of the central ion alone and not to co-ordination electrons combining the central atom to the ligands.

(b) The second absorption band: This may be explained as due to a kind of incomplete dissociation of the complex radical by irradiation. Showing the excited states of the co-ordination electrons, therefore, this band may be considered as giving the measure of stability of complex salts or co-ordination compounds in a wider sense.

(c) The third absorption band: This appears, when (i) a pair or pairs of negative ligands are situated in trans-positions to each other in octahedral or square complex radicals, e.g., $[Co(NH_3)_4Cl_2^{(1)}_{(6)}]^+$[6] and $[Co(NH_3)_4(NO_2)_2^{(1)}_{(6)}]^+$[7] or $[Ni(CN)_4]^{--}$[8], and (ii) two or more negative ligands are co-ordinated around the central ion in tetrahedral complex radicals such as chromate ion, CrO_4^{--}[3].

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(1) R. Tsuchida, this Bulletin, **13** (1938), 388.
(2) R. Tsuchida, *ibid.*, **13** (1938), 436.
(3) R. Tsuchida, *ibid.*, **13** (1938), 471.
(4) R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 733; S. Kashimoto, R. Tsuchida, *ibid.*, **60** (1939), 347.
(5) R. Luther, A. Nikolopulos, Z. *physik. Chem.*, **82** (1913), 361.
(6) R. Tsuchida, this Bulletin, **11** (1936), 721.
(7) Y. Shibata, *J. Chem. Soc. Japan*, **36** (1915), 1243.
(8) H. Kuroya, R. Tsuchida, *ibid.*, **61** (1940), 597.

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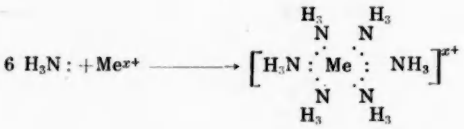
(d) The special absorption band: This band found in special cases is due to absorption band proper to the ligand itself[3], or to a new strongly absorbing centre[2] which has been formed by co-ordination of the particular ligand.

These conclusions have been reached by one of the authors after a series of experimental works and the results have been carefully developed to explain absorption spectra of various compounds, inorganic and organic.

II. On Ethylenediamine Complex Salts: It is a well-known fact that the complex salt of ethylenediamine, which can be regarded as a substitution product of the corresponding ammine complex, is much more stable than the ammine salt, although their colours are similar to each other. For example, praseo-cobalti-salt $[Co(NH_3)_4Cl_2\{^{(1)}_{(6)}\}]X$ is decomposed faster in aqueous solutions than the corresponding ethylenediamine salt $[Co\,en_2Cl_2\{^{(1)}_{(6)}\}]X$. Of the two possible isomers of $[Co(NH_3)_4(H_2O)_2]X_3$ only cis-diaquo-salt is known, whereas in the more stable diaquo-ethylenediamine-compounds both the cis- and the trans-forms have been obtained.

Ammonia forms ammine complexes, being co-ordinated around the central atoms by its lone pair of electrons, and such an interpretation can be adopted also for the formation of ethylenediamine complexes: thus



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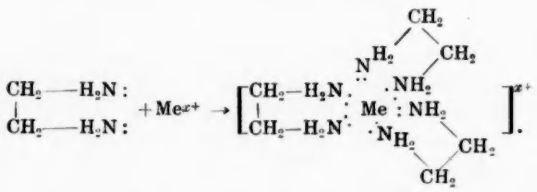


The similarity between properties of ammine salts and those of the corresponding ethylenediamine complexes may thus be understood.

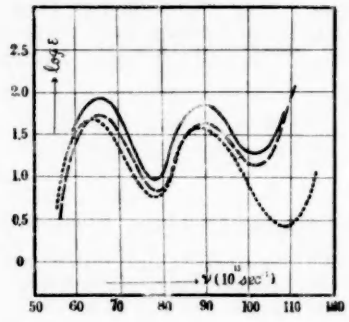
According to the postulates proposed by the authors, however, we can expect a shift of the second absorption band of ethylenediamine complex towards the more spectrally stable direction, or in other words, the shorter wave-lengths, compared with the less stable ammine salt.

For the purpose of confirming this point of view, the authors have prepared fourteen ethylenediamine complex salts and investigated their absorption spectra, comparing them with those of the corresponding ammine salts, which had been measured in this laboratory. In this paper the results of these experiments are dealt with, and the bearings of the observations on the problem of configuration or chemical combination will be discussed.

Experimental Results and Discussions. The experimental results are summarized in Table 1, while the absorption curves thus obtained are shown in Fig. 1–12 together with those of the corresponding ammine complexes for the purpose of comparison.

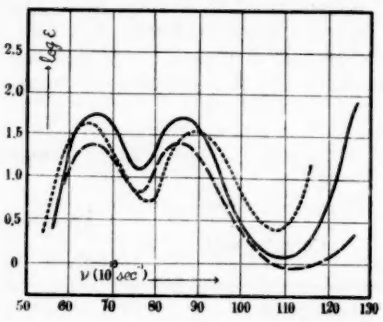
Table 1.

Complex salt	First band		Second band		Third band		Special band	
	$\nu_1(10^{13})$	log ε	$\nu_2(10^{13})$	log ε	$\nu_3(10^{13})$	log ε	$\nu_s(10^{13})$	log ε
$[Co(NH_3)_6]\,Cl_3$	63.2	1.66	88.8	1.58				
$[Co\ en_2\ (NH_3)_2^{(1)}_{(6)}]\,Br_3$	64.8	1.72	89.2	1.62				
$[Co\ en_3]\,Br_3$	64.6	1.88	89.2	1.81				
$[Cr(NH_3)_6]\,Cl_3$	65.0	1.44	85.4	1.45				
$[Cr\ en_3]\,Cl_3$	66.0	1.78	85.6	1.75				
$[Co(NH_3)_5\,Cl]\,Cl_2$	58.0	1.65	83.1	1.66				
$[Co\ en_2\ NH_3\ Cl^{(1)}_{(2)}]\,Cl_2$	58.0	1.76	83.0	1.76				
$[Co\ py_4\ NH_3\ Cl]\,Cl_2$	56.8	1.95	82.6	1.93				
$[Co(NH_3)_4\ (NO_2)_2^{(1)}_{(6)}]\,Cl$	67.9	2.32	87.0	3.54	119.6	4.08	?	?
$[Co\ en_2\ (NO_2)_2^{(1)}_{(6)}]\,NO_3$ ✓	69.9	2.20	88.6	3.44	120.4	4.37	?	?
$[Co(NH_3)_4\ (NO_2)_2^{(1)}_{(2)}]\,Cl$	65.5	1.99	91.2	3.10			?	?
$[Co\ en_2\ (NO_2)_2^{(1)}_{(2)}]\,NO_3$ ✓	69.0	2.10	92.8	3.68			?	?
$[Co(NH_3)_4Cl.NO_2^{(1)}_{(6)}]\,Cl$	63.2	1.87	88.8	3.13	123.0	4.07	(80.4)	(2.42)
$[Co\ en_2\ Cl.NO_2^{(1)}_{(6)}]\,Cl$	68.8	2.00	89.6	3.37	124.2	4.35	(79.6)	(2.22)
$[Co\ en_2\ Cl.NCS^{(1)}_{(2)}]\,Cl$	59.6	2.18	(88.4)	(2.75)			?	?
$[Co\ en_2\ Cl.NCS^{(1)}_{(6)}]\,Br$	54.0	2.10	(86.8)	(2.93)	110.4	3.43	92.5	3.36
$[Co\ en_2\ NO_2.NCS^{(1)}_{(2)}]\,Cl$	64.8	2.34	?	?			?	?
$[Co\ en_2\ NO_2.NCS^{(1)}_{(6)}]\,NCS$	65.3	2.30	?	?	?	?	?	?
$[Co\ (NH_3)_4CO_3]\,Cl$	57.4	2.03	82.8	2.02				
$[CO\ en_2\ CO_3]\,Cl$	58.6	2.08	83.6	2.04				
$[Co\ (NH_3)C_2O_4]\,Cl$	59.0	1.78	83.4	1.78				
$[Co\ en_2C_2O_4]\,Br$	60.0	1.96	84.2	2.10				
$\left[Co\left\{\begin{matrix}OH\\OH\end{matrix}\right\rangle Co\,(NH_3)_4\right\}_3\Big]\,Cl_6$	60.8	2.28	?	?			99.2	3.84
$\left[Co\left(\begin{matrix}OH\\OH\end{matrix}\right\rangle Co\ en_2\right)_3\Big]\,(NO_3)_6$	61.2	2.44	?	?			99.0	3.82
$\left[(NH_3)_4\,Co\left\langle\begin{matrix}OH\\OH\end{matrix}\right\rangle Co\,(NH_3)_4\right]Cl_4$	57.0	2.28	79.2	2.40			107.4	3.34
α-$[Co(glycine)_3]$	56.8	1.98	81.0	2.16				



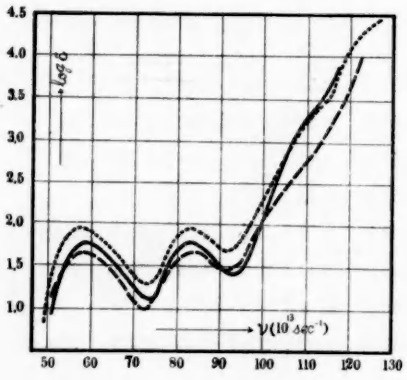
(1) ——— $[Co\ en_3]Br_3$
(2) – – – – $[Co\ en_2(NH_3)_2{}^{(1)}_{(6)}]Br_3$
(3) ····· $[Co(NH_3)_6]Cl_3$

Fig. 1.



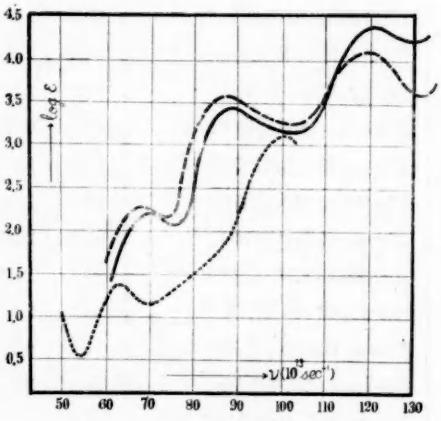
(1) ——— $[Cr\ en_3]Cl_3$
(2) – – – – $[Cr(NH_3)_6]Cl_3$
(3) ····· $[Co(NH_3)_6]Cl_3$

Fig. 2.



(1) ——— $[Co\ en_2NH_3Cl{}^{(1)}_{(2)}]Cl_2$
(2) – – – – $[Co(NH_3)_5Cl]Cl_2$
(3) ····· $[Co\ py_4NH_3Cl]Cl_2$

Fig. 3.

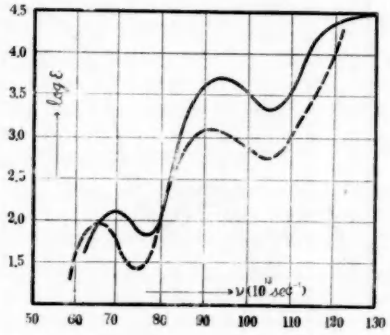


(1) ——— $[Co\ en_2(NO_2)_2{}^{(1)}_{(6)}]NO_3$
(2) – – – – $[Co(NH_3)_4(NO_2)_2{}^{(1)}_{(6)}]Cl$
(3) ····· $[Co\ en_2Cl_2{}^{(1)}_{(6)}]Cl$

Fig. 4.

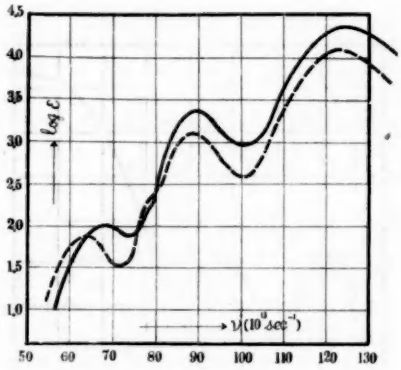
There can be found distinct shifts of both the first, the second, and even the third absorption band in most cases towards the shorter wavelengths in ethylenediammine compounds compared with the corresponding ammine salts. In a few cases, these bands have frequencies equal to those of the corresponding ammine salts. It is also noteworthy that in nearly all the ethylenediamine salts, their extinction coefficients are larger than those of the ammine salts.

Now, when we compare the absorption spectra of $[Co\ en_3]Br_3$ and less stable $[Cr\ en_3]Cl_3$, it can be found that the first absorption band



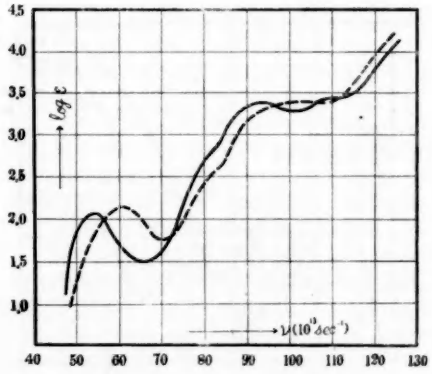
(1) ——— [Co $en_2(NO_2)_2^{(1)}_{(2)}$]NO_3
(2) – – – – [$Co(NH_3)_4(NO_2)_2^{(1)}_{(2)}$]Cl

Fig. 5.



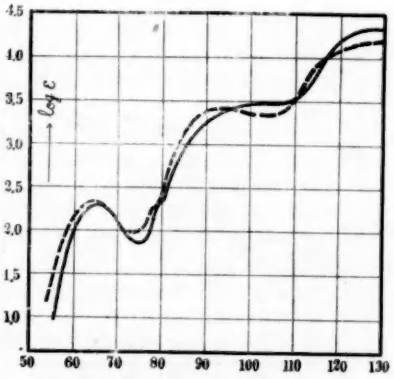
(1) ——— [Co $en_2Cl \cdot NO_2^{(1)}_{(6)}$]Cl
(2) – – – – [$Co(NH_3)_4Cl \cdot NO_2^{(1)}_{(6)}$]Cl

Fig. 6.



(1) ——— [Co $en_2Cl \cdot NCS^{(1)}_{(6)}$]Br
(2) – – – – [Co $en_2Cl \cdot NCS^{(1)}_{(2)}$]Cl

Fig. 7.

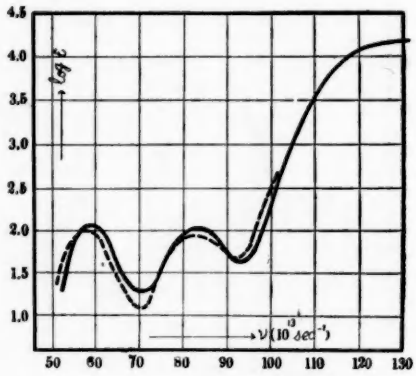


(1) ——— [Co $en_2NO_2 \cdot NCS^{(1)}_{(6)}$]NCS
(2) – – – – [Co $en_2NO_2 \cdot NCS^{(1)}_{(2)}$]Cl

Fig. 8.

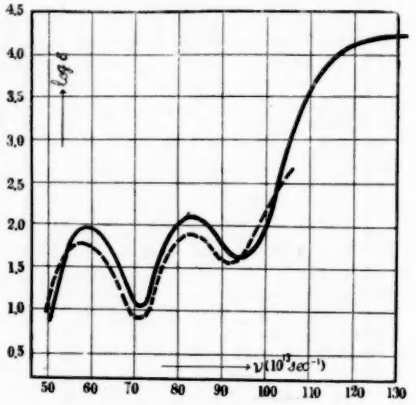
of the Cr^{III}-salt has shorter wave-lengths, while the second band of the Co^{III}-salt is, on the contrary to the first band, more hypsochromic than the Cr^{III}-salt. Similar relation can be seen for $[Co(NH_3)_6]Cl_3$ and $[Cr(NH_3)_6]Cl_3$. Such positions of the bands may be regarded as a proof of the validity of the author's hypothesis stated above, that the second absorption band is a scale for the stability of co-ordination compound. while the first absorption band is unqualified to be so. It is an important fact that the luteo-Co^{III}-salts are, despite of their more intense colours, not inferior in the stability to the luteo-Cr^{III}-salts, in agreement with the order of their second absorption bands.

In the following, the individual cases will be described.



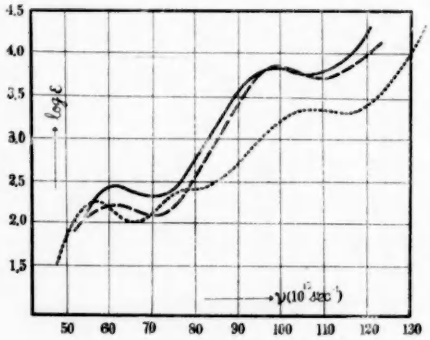
(1) ——— [Co en$_2$CO$_3$]Cl
(2) – – – – [Co(NH$_3$)$_4$CO$_3$]Cl

Fig. 9.



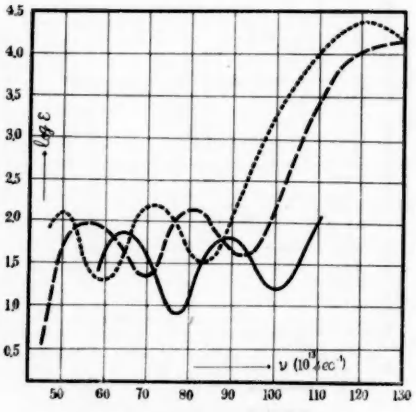
(1) ——— [Co en$_2$C$_2$O$_4$]Br
(2) – – – – [Co(NH$_3$)$_4$C$_2$O$_4$]Cl

Fig. 10.



(1) ——— [Co$\left(\begin{matrix}OH\\OH\end{matrix}\right>$Co en$_2\Big)_3$](NO$_3$)$_6$
(2) – – – – [Co$\left\{\begin{matrix}OH\\OH\end{matrix}\right>$Co(NH$_3$)$_4\Big\}_3$]Cl$_6$
(3) ·····- [(NH$_3$)$_4$Co$\left<\begin{matrix}OH\\OH\end{matrix}\right>$Co(NH$_3$)$_4$]Cl$_4$

Fig. 11.



(1) ——— [Co en$_3$]Br$_3$
(2) – – – – [Co(glycine)$_3$]
(3) ------- K$_3$[Co(C$_2$O$_4$)$_3$]

Fig. 12.

(i) Luteo-salts: Showing the absorption bands of the almost identical frequency, the stabilities of [Co(NH$_3$)$_6$]Cl$_3$, [Co en$_2$(NH$_3$)$_2\{^{(1)}_{(6)}\}$]Br$_3$ and [Co en$_3$]Br$_3$ are equal to each other. The case is also similar in the luteo-Cr^{III}-salts.

(ii) Purpureo-salts: Three salts, [Co(NH$_3$)$_5$Cl]Cl$_2$, [Co en$_2$NH$_3$ Cl$\{^{(1)}_{(2)}\}$]Cl$_2$ and [Co py$_4$NH$_3$Cl]Cl$_2$, are of the almost identical colour, and in fact, the first and the second bands of them lie in practically the same positions respectively. With regard to the configuration of the tetrapyridine salt, there are two possible cases, namely cases of cis- and trans-

configurations, concerning the positions of NH_3-molecule and Cl-ion. It is difficult, however, to decide whether this salt has cis- or trans-configuration, only from the absorption spectrum. In the present state, the cis-form is more probable, because this salt can be prepared by interaction of aqueous ammonia with $[Co\,py_4Cl_2]Cl$, which, according to A. Werner[9], has its Cl-ions in trans-positions, and, therefore, by entirely the same procedure as in the preparation of $[Co\,en_2NH_3Cl^{(1)}_{(2)}]Cl_2$ from the praseo-salt $[Co\,en_2Cl_2^{(1)}_{(6)}]Cl$.

(iii) Croceo-salts: It will be found that the third absorption band of the ethylenediamine salt can be observed distinctly in the region of $\nu=120-130$, overlapping with the special band due to the co-ordinated ethylenediamine molecules, while the ammine croceo-salt is well known to be an example for the salt having the third absorption band. By comparing the absorption curves of both the salts, we can see that every member of the three bands is much more stabilized by the remarkable shift towards the shorter wave-lengths in the ethylenediamine compound, compared with the ammine salt.

It will be added, moreover, that the special absorption band due to the co-ordinated nitro-radicals[10] could not be distinguished from the second band.

(iv) Flavo-salts: Comparing the absorption of $[Co(NH_3)_4(NO_2)_2^{(1)}_{(2)}]Cl$ and $[Co\,en_2(NO_2)_2^{(1)}_{(2)}]NO_3$, we can observe shifts of both the first and the second band to the side of shorter wave-lengths in the latter.

A hump of the absorption curve of the ethylenediamine salt in the region of $\nu=120-130$ is attributed to the selective absorption proper to the co-ordinated ethylenediamine molecules, and the third absorption band due to trans-negative radicals is naturally out of question here.

(v) 1,6-Chloro-nitro-salts: $[Co\,en_2Cl.NO_2^{(1)}_{(6)}]Cl$ has been proved to have the third band in the present work, while the third band of the corresponding ammine salt had been reported previously[11]. The special absorption bands proper to the nitro-radicals are illustrated here; they can be seen approximately at $\nu=80$. Regarding the relative positions, the bands of the ethylenediamine salt seem more hypsochromic.

(vi) Chloro-rhodanato-salts: Of the two possible isomers, cis- and trans-form, the latter ought to have a third band, because of co-ordination of the negative ligands in trans-positions. A small band at $\nu=110.4$ may be assigned to it. On the other hand, one special band due to the co-ordinated rhodanato-radical is to be expected for each of them, and then inflection of their absorption curves in the middle between $\nu=80$ and 90 can be explained as the results of overlapping of the special bands upon the second bands.

It is regretable that there do not exist the ammine salts corresponding to either of the two isomers of $[Co\,en_2Cl.NCS]X$.

For the interesting problem, which of the two isomers is more stable, no answer can be given from the spectra alone, as their second bands are unable to be determined.

(9) A. Werner, R. Feenstra, *Ber.*, **39** (1906), 1538.
(10) H. Kuroya, R. Tsuchida, *J. Chem. Soc. Japan*, **59** (1938), 1142.
(11) R. Tsuchida, S. Kashimoto, this Bulletin, **11** (1936), 785.

(vii) Nitro-rhodanato-salts: In these, there will be expected several absorption bands, namely, the first, the second, and the special bands due to the co-ordinated nitro- und rhodanato-radicals in the case of cis-form, and moreover, in addition to them, the third absorption band in the case of trans-form. In reality, however, only the first bands can be distinguished in the both isomers, surely because of complex superposition of these bands.

(viii) Tetrammine-carbonato- and -oxalato-salts: It can be seen obviously from Figs. 8 and 9 that the ethylenediamine compound is more stable in every set of carbonato- and oxalato-salts, for the bands, especially the second, are more hypsochromic in the ethylenediamine compounds.

(ix) Hexol-salts: With regard to the first bands only, which are distinct in both the ammine and the ethylenediamine salt, the latter is more hypsochromic than the former. The second bands, however, could not be discriminated due to their complex configurations.

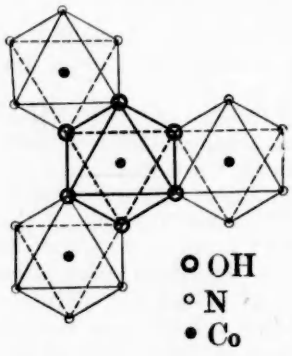


Fig. 13. Configuration of hexol-salt.

At the beginning of the present work, we expected the existence of a third absorption band in hexol-salts, because OH-radicals as many as six are co-ordinated around the innermost Co-atom, forming thus three pairs of trans-anions. The bands having their absorptive maxima nearly at $\nu=99$, however, should not be considered as the expected third bands, for there is a similar band in the absorption curve of the diol-salt, which is not at all qualified to possess its third band. Such being the case, the absence of the third absorption band of hexol-salts seemed to be difficult to explain at first sight. The lack of the third band in hexol-salts, however, may be understood by comparing them with aquo-complex salts; the OH-radical in hexol salts are quite similar to the OH_2-molecule in aquo-salts, with regard to the co-ordinative behaviour of the O-atom which has three ligands, two hydrogen atoms and one metallic ion in the aquo-salts and one hydrogen atom and two metallic ions in hexol-salts.

In addition, a few words may be said of the questionable bands at $\nu\approx99$; the present authors would like to explain these as being due to co-ordination of the ligands around the central O-atoms, because Prof. Tsumaki[12] had shown previously the appearances of similar bands in some of organic complex salts.

(x) α-[Co(glycine)$_3$] (violet form): Two forms are theoretically possible for cobaltic triglycine: cis-cis- and cis-trans-form (Fig. 14). In fact, Ley and Winkler[13] had prepared these two isomers. A question, however, is left unsolved, which of the two isomers, violet α- or red β-form, is to be a cis-cis-, and the other a cis-trans-form. Attempting to solve this problem, the present authors have measured the absorption of the

(12) R. Tsuchida, T. Tsumaki, this Bulletin, **13** (1938), 527.
(13) H. Ley, H. Winkler, *Ber.*, **42** (1909), 3900.

violet form only, the red form being unavailable for measurements because of its insolubility in water. Now, were the violet form a cis-trans-form, its absorption curve would show a third band on account of the carboxyl radicals distributed in trans-positions.

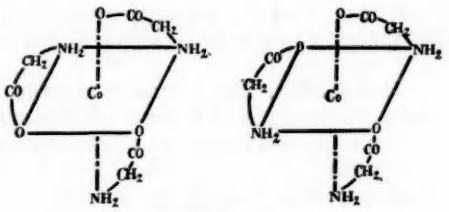
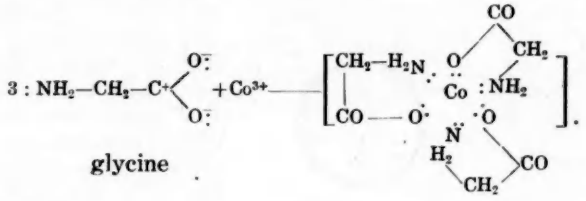


Fig. 14.

In the present work, however, no band was detected, which might be described as the third band. This may be considered as a favorable proof for the cis-cis-configuration.

It is well known that a molecule of α-amino acid can co-ordinate itself to an ion of heavy metals, e.g., Cu^{++}, Co^{3+}, etc., in order to form the so-called "inner complex", which is usually insoluble in water. Co-ordination must take place through the agency of its lone pairs of electrons, which belong to the NH_2-radical and the oxygen atoms of carboxyl radical; thus:



glycine

Accordingly, apart from the configuration referred to above, it may be reasonable to consider, that cobaltic triglycine is intermediate between $[Co\,en_3]^{3+}$ and $[Co(C_2O_4)_3]^{3-}$, concerning the modes of co-ordinative combinations.

Hereupon, it is desirable to compare the absorption spectra of those salts. In Table 2, the frequencies, at which they show the maximum ε-values respectively, are tabulated, and their absorption curves are arranged side by side in Fig. 12.

Table 2.

Complex Salt	First band ν_1 (10^{13})	Second band ν_2 (10^{13})	Third band ν_3 (10^{13})
$[Co\,en_3]Br_3$	64.6	88.2	—
$[Co(glycine)_3]$	56.8	81.0	—
$K_3[Co(C_2O_4)_3]$[14]	49.6	71.0	122.4

As can be seen from the table as well as the figure, the triglycine compound in question lies intermediate between the other two, offering

(14) S. Kashimoto, M. Kobayashi, this Bulletin, **12** (1937), 350.

an obvious proof for the supposition that the chemical combination through a N-Co-bond might be stronger than that through a O-Co-bond.

Conclusion. By summarizing the results obtained above, it is confirmed decisively a hypothesis of the authors, that the second absorption band may be attributed to co-ordination electrons combining the central atom to the ligands, and, therefore, the stability of the co-ordination compound may be measured by its second absorption band, because the second band of ammine complex is, in general, more bathochromic than that of the corresponding ethylenediamine salt which is practically much more stable.

Then, it must come into question, why the ethylenediamine complexes are more stable in these ways. If a linkage of N-C-C-N of an ethylenediamine molecule is supposed to be on a plane, a simple calculation indicates the N-N-distance as equal to 2.5Å., assuming the atomic radius R_N=0.7 and R_C=0.77Å.[15], while, on an assumption of R_{Co}=1.22Å.[15] and the angle N-Co-N=90°, N-N must have the value 2.7Å. An ethylenediamine molecule, therefore, can be easily co-ordinated to a central cobalt atom, if a little distortion would be permitted around its bonds. According to P. Trunel's measurement[16] of dipole moment, there are completely free rotations around the C-C- and C-N-bond in an ethylenediamine molecule. Under this circumstance, the co-ordinating procedure will be very smooth and steady[17].

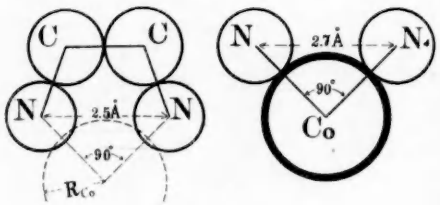


Fig. 15.

In addition to this condition, the both ends of ethylenediamine molecule are bonded to the central atom, making thus the combination in the co-ordination sphere much more poor in chances of its being broken out than in ammine complex, in which every member of the co-ordinated NH_3-molecules is singly bonded to the central atom.

Experimental. (1) Diethylenediamine cobaltic complexes: Prepared by the methods of A. Werner[18] by the processes shown in Table 3.

(2) $[Co\,en_3]Br_3.3H_2O$ (Luteo-cobaltic-salt): This salt can be synthesized by use of $[Co(NH_3)_5Cl]Cl_2$ and ethylenediamine with facility, but also will be obtained in a comparatively good yield as a by-product, when the praseo-salt $[Co\,en_2Cl_2^{(1)}_{(6)}]Cl$, which is a starting substance of the diethylenediamine series, is prepared. The authors' method of separation from a mixture of the luteo- and the praseo-salt is given in Table 4.

(15) L. Pauling, "The Nature of the Chemical Bond", 2nd Ed., 164 and 182, New York (1940).
(16) P. Trunel, *Compt. rend.*, **203** (1936), 563.
(17) Cf. J. P. Mathieu, *Bull. soc. chim.*, **5** (1938), 749.
(18) A. Werner, *Ann.*, **386** (1912), 1.

Table 3.

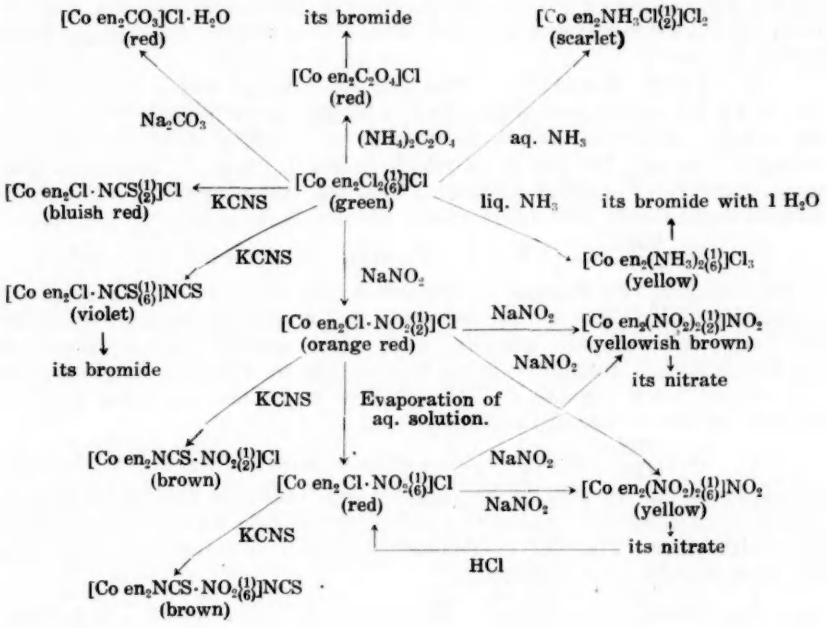
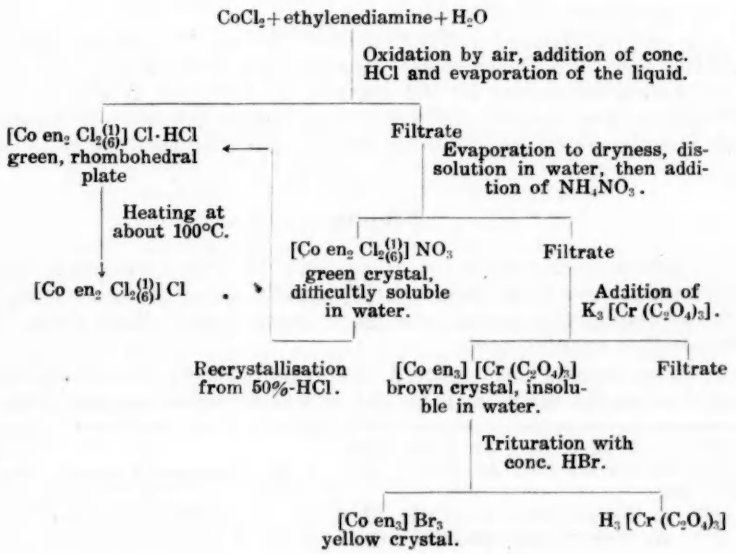


Table 4.


CoCl2 + ethylenediamine + H2O
Oxidation by air, addition of conc. HCl and evaporation of the liquid.
[Co en2 Cl2(1)(6)] Cl·HCl
green, rhombohedral plate
Filtrate
Evaporation to dryness, dissolution in water, then addition of NH4NO3.
Heating at about 100°C.
[Co en2 Cl2(1)(6)] NO3
green crystal, difficultly soluble in water.
Filtrate
[Co en2 Cl2(1)(6)] Cl
Addition of K3 [Cr (C2O4)3].
Recrystallisation from 50%-HCl.
[Co en3] [Cr (C2O4)3]
brown crystal, insoluble in water.
Filtrate
Trituration with conc. HBr.
[Co en3] Br3
yellow crystal.
H3 [Cr (C2O4)3]

(3) $[Cr\,en_3]Cl_3.3.5H_2O$ (Luteo-chromic-salt): Pfeiffer[19] had prepared this salt, using ethylenediamine hydrate and partially dehydrated, grey-coloured chrome alum. The authors followed his method. Both the luteo-Cr-salt and the luteo-Co-salt are yellow, the former being lighter in hue.

(4) $[Co\,py_4NH_3Cl]Cl_2$: This can be obtained, being derived from $[Co\,py_4Cl_2]Cl$, which was originally synthesized by A. Werner[9] by oxidising a cold solution of cobaltous chloride in pyridine with chlorine; the tetrapyridine salt, the colour of which is bluish green, is tritulated with small quantity of aqueous ammonia, then the chloro-ammine salt may be formed immediately, causing a colour change from green to violet-red.

(5) $[Co\left\{\begin{matrix}OH\\OH\end{matrix}\right\rangle Co(NH_3)_4\Big\}_3]Cl_6.2H_2O$ (Hexol-salt): According to the method given by Werner[20], tetrammine chloro-aquo-cobaltic sulphate, $[Co(NH_3)_4Cl.H_2O]SO_4$, was dissolved in a closed vessel containing 10% aqueous ammonia solution, and, after several hours, there was found the aimed, difficulty soluble hexol-sulphate, forming flat, scale-like and almost black crystals. This sulphate was then converted into its chloride by use of barium chloride.

(6) $[Co(\begin{matrix}OH\\OH\end{matrix}\rangle Co\,en_2)_3](NO_3)_6.3H_2O$ (Ethylenediamine hexol-salt): Prepared by the method of Werner[21], who obtained this hexol-salt by oxidation of a solution containing cobaltous nitrate and ethylenediamine in an airy place. This salt is considerably richer in brownish colour than the corresponding ammine-hexol.

(7) $[(NH_3)_4Co<\begin{matrix}OH\\OH\end{matrix}>Co(NH_3)_4]Cl_4.4H_2O$ (Diol-salt: The sulphate was prepared by the method of Werner[22], a dehydration of tetrammine hydroxo-aquo-cobaltic sulphate, $[Co(NH_3)_4H_2O.OH]SO_4$, at temperatures between 100 and 110°, and this diol-sulphate was converted into its chloride by use of barium chloride.

(8) α-$[Co(glycine)_3].2H_2O$ (violet form): Cobaltic hydroxide, $Co(OH)_3$, and pure glycine were together boiled in aqueous solution for several hours, according to the method of Ley and Winkler[13]. One modification thus formed, the red β-form, being insoluble in water, the liquid was filtered off and from this could be crystallised the violet α-salt.

Summary.

1. Absorption spectra of a number of ethylenediamine cobaltic complex salts have been observed. Generally speaking, their absorption bands, especially the second, are more hypsochromic than those of the corresponding ammine salts.

2. The results have proved that the author's hypothesis on the absorption spectra holds good for the ethylenediamine complex salts.

(19) P. Pfeiffer, *Ber.*, **37** (1904), 4277.
(20) A. Werner *Ber.*, **47** (1914), 3087; S. M. Jörgensen, *Z. anorg. Chem.*, **16** (1898), 186.
(21) A. Werner, *Ber.*, **40** (1907), 2119.
(22) A. Werner, *ibid.*, **40** (1907), 4437.

3. Examples of the third absorption bands have been found in the diethylenediamine cobaltic complexes of known configurations.

4. A new method of separating $[Co\,en_3]^{3+}$ and $[Co\,en_2Cl_2^{(1)}_{(6)}]^+$ has been devised.

Department of Chemistry, Faculty of Science,
Osaka Imperial University.

Copper, Lead, and Zinc Content of the Hot Springs of Japan.

By Kazuo KURODA.

(Received September 25, 1940.)

The occurrence of copper in a large number of hot springs of Japan has been found spectroscopically by K. Kimura[1] and in the present work a method for the determination of the minute quantities of copper in the large amounts of iron was studied and the method was applied to the determination of the element in a number of mineral springs of Japan. The copper, lead, and zinc content of some weak alkaline hot springs were also estimated by Fischer's method[2].

I. Determination of the Minute Quantities of Copper in the Mineral Springs. Add nitric acid to a 500 c.c. portion of the mineral water and boil to oxidize the iron to the ferric condition. Add ammonium hydroxide (1:1) to slight excess and 5 c.c. of saturated ammonium carbonate solution. Warm and filter. Wash the residue with a warm mixture of 10 c.c. of water, 1 c.c. of ammonium hydroxide (1:1) and 1 c.c. of saturated ammonium carbonate solution. Dissolve the precipitate in 5 c.c. of nitric acid (1:5) and precipitate as above. Combine the filtrates, and render them acid with dilute nitric acid and evaporate to dryness.

Dissolve the residue in nitric acid, ajust to *p*H 3 and titrate with the carbon tetrachloride solution of dithizone. The orange yellow colour of the carbon tetrachloride layer indicates the presence of silver. The silver is removed until the carbon tetrachloride layer turns to reddish violet. The carbon tetrachloride solution of dithizone is added with small portions until it remains green when vigorously shaken for several minutes. The amount of copper is obtained from the volume of the carbon tetrachloride solution of dithizone used to extract the reddish violet dithizone complex of copper. Each c.c. of the dithizone solution corresponded to 2.5γ of copper.

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(1) Not yet published.
(2) H. Fisher, *Angew. Chem.*, **47** (1934), 685; **50** (1937), 919. etc.

II. Copper Content of Some Mineral Springs of Japan.

The results from the quantitative determination of the minute traces of copper in some mineral springs of Japan is shown in Table 1. The iron content of some of these mineral springs was determined gravimetrically or by Mellor's colorimetric method, and the atomic ratio of copper to iron in the mineral springs was calculated (Table 2).

Table 1. Copper Content of Some Mineral Springs of Japan.

No.	Mineral spring	Prefecture	Temperature (°C)	*p*H	Copper Content	
					(γ/l.)	% (total residue.)
1	Kinbu	Yamanasi	—	—	68000	0.15
2	Kinkei	Totigi	10.0	2.4	1033	0.050
3	Daruma-Zigoku, Yunohanazawa, Hakone.	Kanagawa	93.0	2.0	163	0.0081
4	Hon-Onsen, Arima	Hyōgo	—	—	140	0.00084
5	Kinkei No. 2	Totigi	8.7	2.9	140	—
6	Yoemon-Yu, Yunohanazawa, Hakone.	Kanagawa	87.8	2.2	90	0.0053
7	Yagendo, Arima.	Hyōgo	—	—	38	0.00035
8	Iron spring No. 1, Sinyu, Sukayu.	Aomori	—	—	12	—
9	Iron spring No. 2, Sinyu, Sukayu.	Aomori	—	—	10	—
10	Gongen-Yu, Yunohanazawa, Hakone.	Kanagawa	51.0	2.5	10	0.0010
11	Cold spring near Kinkei.	Totigi	6.0	6.5	6	—

Table 2. Atomic Ratio of Copper to Iron.

No.	Mineral Spring	Iron Content (g./l.)	Atomic Ratio of Copper to Iron. (Cu : Fe)
1	Kinbu	10.416	1 : 174
2	Kinkei	0.177	1 : 196
3	Daruma-Zigoku	0.016	1 : 112
4	Hon-Onsen	0.030	1 : 242
5	Kinkei No. 2	—	—
6	Yoemon-Yu	0.157	1 : 1980
7	Yagendo	—	—
8	Iron Spring No 1	0.00015	1 : 14
9	Iron Spring No. 2	—	—
10	Gongen-Yu	0.0068	1 : 777
11	Cold Spring near Kinkei	—	—

III. Copper, Lead, and Zinc Content of a Number of Weak Alkaline Hot Springs of Japan. The copper, lead, and zinc content of a number of weak alkaline hot springs in Japan were estimated by the colorimetric method. For the determination of lead, the colorimetric method which was described in the previous paper[3] was used. For the colorimetric determination of zinc, H. Fisher and G. Leopoldi's method[4] was adopted. The results of the experiments are shown in Table 3. Copper was detected in three samples (out of twelve samples), and lead in two samples (out of twelve samples). The traces of zinc were always found in these hot springs. The average zinc content of twelve samples was 13γ per litre.

Table 3. Copper, Lead, and Zinc Content of Some Hot Springs of Japan.

No.	Hot Spring	Prefecture	Temperature (°C)	*p*H	Cu	Pb (mg/l.)	Zn
1	Itō No. 3	Sizuoka	42.0	8.0	0.000	0.033	0.009
2	Itō No. 4	,,	42.0	8.0	0.003	0.000	0.015
3	Itō No. 8	,,	40.5	7.3	0.003	0.002	0.008
4	Itō No. 10	,,	38.0	7.4	0.002	0.000	0.010
5	Itō No. 13	,,	40.5	7.4	0.000	0.000	0.008
6	Moto-Yu, Kawazi	Totigi	43.0	7.7	0.000	0.000	0.009
7	Komoti-Yu, Kawazi	,,	43.0	7.7	0.000	0.000	0.021
8	Iwa-no-Yu, Kawazi	,,	42.5	7.7	0.000	0.000	0.027
9	Yakusi-Yu, Kawazi	,,	43.0	7.7	0.000	0.000	0.024
10	Hudō-no-Yu, Kawazi	,,	40.2	7.7	0.000	0.000	0.025
11	River Water, Ozikagawa, Kawazi	,,	15.5	7.1	0.000	0.002	0.036
12	Takara-no-Yu, Kinugawa	,,	55.5	8.0	0.000	0.000	0.012
13	Senami	Niigata	100.3	8.7	0.000	0.000	0.010
14	Sea Water, Itō	Sizuoka	—	—	0.009	0.004	0.006
15	Sea Water, Senami	Niigata	—	—	0.010	0.001	0.008

Summary.

(1) A method for the determination of the minute quantities of copper in the mineral springs was studied.

(2) Copper, lead, and zinc content of a number of hot springs of Japan were estimated.

The author expresses his hearty thanks to Prof. Kenjiro Kimura for his kind guidance. The expense for the experiments has been defrayed from a grant given to Prof. Kimura by the Japan Society for the Promotion of Scientific Research, to which the author's thanks are due.

Chemical Institute, Faculty of Science,
Imperial University of Tokyo.

(3) K. Kuroda, this Bulletin, **15** (1940), 153.
(4) H. Fischer and G. Leopoldi, *Z. anal. Chem.*, **107** (1936), 241.

The Addition of Hydrogen Bromide to Cholesteryl Bromide and the Oxygen Effect.

By Yoshiyuki URUSHIBARA, Keiiti NAMBU, and Toshio ANDO.

(Received September 26, 1940.)

The addition of hydrogen bromide to allyl bromide and to undecenoic acid (in toluene) follows the Markownikoff rule[1] in the absence of oxygen and peroxides and gives the normal products, 1,2-dibromopropane and 10-bromoundecanoic acid respectively, in a nearly pure state. The presence of a minute quantity of oxygen in the reacting mixtures causes a reversal of the direction of addition, the abnormal products, 1,3-dibromopropane and 11-bromoundecanoic acid respectively, being formed as the main products. The oxygen effect on the addition of hydrogen bromide has been observed also with many other ethenoid compounds.[2] Further, isostilbene has been found to isomerize to stilbene in the presence of hydrogen bromide and oxygen, but not in the presence of either one of them[3].

One (Y.U.) of the authors and O. Simamura investigated the action of the mixture of hydrogen bromide and oxygen on allyl bromide and on stilbene[4]. The former gave water, free bromine, 1,2,3-tribromopropane, and a peroxide, probably dibromoisopropyl peroxide, besides 1,3-dibromopropane, the main product. The latter yielded stilbene dibromide as the main product, which was accompanied by small amounts of a peroxide and free bromine. From these results they postulated a mechanism of the oxygen effect.

Until recently all the examples of addition reactions showing explicitly the oxygen effect were of the addition of hydrogen bromide to terminal double bonds, and ethenoid compounds such as isoundecenoic acid[5][6], isoundecenol[6], and *cis*- and *trans*-pentene-(2)[7], which belong to the type CH_3-CH=CH-CH_2-R with a well-balanced non-terminal ethylene group, gave equal parts of isomeric addition products irrespective of the conditions of addition, thus making the detection of the oxygen effect impossible. Recently it was demonstrated that trimethylethylene[8] and 2-bromobutene-(2)[9], both with unbalanced non-terminal ethylene groups, are

(1) W. B. Markownikoff, *Ann.*, **153** (1870), 256.

(2) For reviews of works on the oxygen effect compare J. C. Smith, *Chemistry and Industry*, **56** (1937), 833; **57** (1938), 461; *Ann. Rep.*, **1939**, 219.

(3) Y. Urushibara and O. Simamura, this Bulletin, **12** (1937), 507; **13** (1938), 566.

(4) Y. Urushibara and O. Simamura, *ibid.*, **14** (1939), 323. Compare also O. Simamura, *ibid.*, **15** (1940), 292.

(5) P. L. Harris and J. C. Smith, *J. Chem. Soc.*, **1935**, 1108.

(6) E. P. Abraham, E. L. R. Mowat, and J. C. Smith, *ibid.*, **1937**, 948.

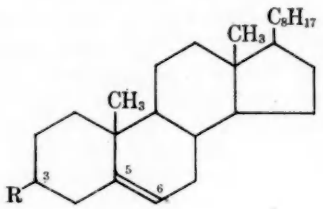
(7) M. S. Kharasch, C. Walling, and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 1559.

(8) C. Walling, M. S. Kharasch, and F. R. Mayo, *ibid.*, **61** (1939), 2693; A. Michael and N. Weiner, *J. Org. Chem.*, **4** (1939), 531.

(9) C. Walling, M. S. Kharasch, and F. R. Mayo, *J. Am. Chem. Soc.*, **61** (1939), 1711.

subject to the oxygen effect when they add hydrogen bromide. The present paper describes the addition of hydrogen bromide to cholesteryl bromide as another example of the hydrogen bromide addition to a non-terminal double bond subject to the oxygen effect.

In cholesterol and other cholestene-(5) derivatives represented by formula I the ethylene group is much unbalanced and carbon atom 5 is sterically much hindered compared with carbon atom 6. Hence, it can be anticipated that the normal addition of hydrogen bromide will produce one isomeride in a predominating proportion while in the presence of oxygen the abnormal addition will yield the other isomeride as the main product, stereoisomerism being disregarded.



(I)

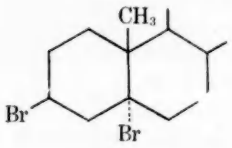
(Ia) R = OH
(Ib) R = Br
(Ic) R = Cl
(Id) R = H
(Ie) R = CH_3CO_2

On treatment with hydrogen bromide, however, cholesterol (Ia) is liable to substitution of a bromine atom for the hydroxyl group[10], and further it has been shown by Ashton and Smith[11] that undecenol, the alcohol corresponding to undecenoic acid, fails to yield an abnormal product under strongly oxidant conditions because of the counter-effect of the hydroxyl group. Cholesteryl halides and cholestene (Id) may be free from such possible difficulties. Thus cholesteryl bromide (Ib) was used for the present investigation, because it is more easily obtainable than cholestene and better suited for the investigation of hydrogen bromide addition than cholesteryl chloride (Ic).

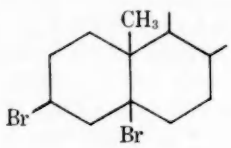
The mechanism of the hydrogen bromide addition as represented in the previous paper[4] requires the hydrogen atom to add to carbon atom 6 and the bromine atom to carbon atom 5 in the normal addition, and in the abnormal addition, if it occurs, the direction of addition of hydrogen bromide to be reversed. Then two stereoisomeric products (IIa and IIb) are possible in the normal addition, because carbon atom 5 becomes asymmetric, and four (IIIa, IIIb, IIIc, and IIId) are possible in the abnormal addition owing to the asymmetry of both carbon atoms 5 and 6. All the possible isomerides, however, may not be obtained in practice. If only one product is obtained in each case, the direction of addition of hydrogen bromide may well be inferred from the examples of simpler ethenoid compounds, but the stereochemical configuration of each product has to be determined.

(10) The action of hydrogen chloride on cholesterol yields 3,5-dichlorocholestane besides cholesterol hydrochloride, J. Mauthner, *Monatsh.*, **27** (1906), 305.

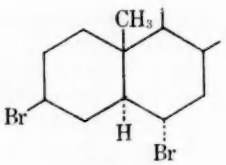
(11) R. Ashton and J. C. Smith, *J. Chem. Soc.*, **1934**, 1308.



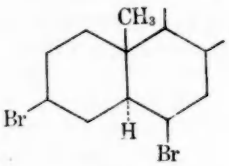
(IIa)



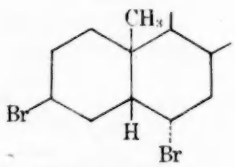
(IIb)



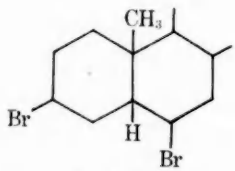
(IIIa)



(IIIb)



(IIIc)



(IIId)

The addition of hydrogen bromide to the cholesterol derivatives represented by formula I has never been studied. Recently Pirrone[12] treated cholesterol with hydrobromic acid in alcoholic solution and obtained an isomeride of cholesterol with small amounts of two substances melting at 120° and 104–105° respectively, which have not been characterized.

There have been many investigations on the addition of hydrogen chloride to cholesterol derivatives. Mauthner[13] obtained a hydrochloride melting at 154–155° from cholesterol and hydrogen chloride. The conversion of it into allocholesterol[14] (IVa) shows that the chlorine atom is situated at carbon atom 5. Fazi[15] obtained several products from the action of hydrogen chloride on cholesterol, but none have been sufficiently characterized. It seems that he doubts the homogeneity of Mauthner's hydrochloride. By the catalytic reduction of cholesterol dichloride Décombe and Rabinowitch[16] obtained a chlorocholestanol, to which they suggested a constitution of 6-chlorocholestanol. It appears that Fazi attributed the same constitution to one of his products[17].

(12) F. Pirrone, *Chem. Zentr.*, **111** (1940), I, 555.

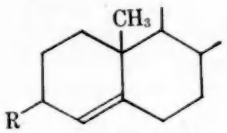
(13) J. Mauthner, *Monatsh.*, **27** (1906), 305.

(14) A. Windaus, *Ann.*, **453** (1927), 101; R. Schoenheimer and E. A. Evans, Jr., *J. Biol. Chem.*, **114** (1936), 567.

(15) R. de Fazi and L. de Fazi-Guerci, *Chem. Zentr.*, **103** (1932), I, 3302; R. de Fazi, *ibid.*, **109** (1938), II, 1781; R. de Fazi and F. Pirrone, *ibid.*, **111** (1940), I, 2652.

(16) J. Décombe and J. Rabinowitch, *Bull. soc. chim.*, [5], **6** (1939), 1510.

(17) *Idem*, *ibid.*, p. 1520.



(IV)

(IVa) R = OH

(IVb) R = H

Mauthner[18] showed the formation of two isomeric hydrochlorides from the addition of hydrogen chloride to cholestene, one of which he isolated in a pure state. As the both hydrochlorides were converted into the same pseudocholestene (IVb), they must be regarded as stereoisomerides both with the chlorine atom at carbon atom 5. The isomeric 6-chlorocholestane was not formed from hydrogen chloride and cholestene but obtained from cholestanol-(6).[19]

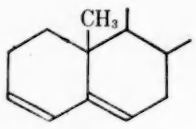
From cholesteryl chloride and hydrogen chloride Mauthner[13] obtained 3,5-dichlorocholestane as the only addition product. The same substance was formed by the action of hydrogen chloride on cholesterol[10]. The isomeric 3,6-dichlorocholestane was obtained by the action of phosphorus pentachloride on cholestanediol-(3,6)[20]. On reduction with sodium and amyl alcohol 3,6-dichlorocholestane gave cholestane.

As summarized above, the addition of hydrogen chloride to cholesteryl chloride gives only one product, while the addition to cholestene and to cholesterol two or more. Thus cholesteryl bromide seemed to be the most suitable substance for the present purpose of studying the addition of hydrogen bromide and the oxygen effect.

The Action of Hydrogen Bromide on Cholesteryl Bromide under the Conditions Favourable for the Normal Addition. The action of hydrogen bromide on cholesteryl bromide in carbon tetrachloride with the addition of a small amount of catechol and the purification of the product gave a crystalline substance showing a melting point 101.5° (corr.), $[\alpha]_D$ + 5.36°, and a bromine content corresponding to the addition of a molecule of hydrogen bromide. The addition in the presence of ferric chloride which is known as an accelerating agent for the normal addition, and the addition in ethereal solution, yielded the same substance. Thus, it is evident that this hydrobromide is the normal product, the bromine atom being situated at carbon atom 5 (IIa or IIb).

The optical rotation affords a further evidence that the hydrobromide corresponds to the addition products of hydrogen chloride to cholesterol, cholestene, and cholesteryl chloride: According to Mauthner[21] the laevorotation of these substances is converted into dextro-rotation by the addition of hydrogen chloride. Cholesteryl bromide is laevo-rotatory ($[\alpha]_D$−20.8°)[22], and the hydrobromide formed by the addition of hydrogen bromide under conditions mentioned above is dextro-rotatory. (The other hydrobromide described below is laevo-rotatory.)

(18) J. Mauthner, *Monatsh.*, **28** (1907), 1113.
(19) O. Stange, *Z. physiol. Chem.*, **220** (1933), 34.
(20) A. Windaus, *Ber.*, **50** (1917), 133.
(21) J. Mauthner, *Monatsh.*, **27** (1906), 314, 421.
(22) J. H. Beynon, I. M. Heilbron, and F. S. Spring, *J. Chem. Soc.*, **1936**, 907.



(V)

The hydrobromide melting at 101.5° easily loses one or two molecules of hydrogen bromide: On boiling in acetone it gives cholesteryl bromide and on boiling in pyridine cholestadiene-(3,5) (V).

The Action of Hydrogen Bromide and Oxygen on Cholesteryl Bromide. The mixture of hydrogen bromide and oxygen was passed into a carbon tetrachloride solution of cholesteryl bromide, and the product was purified to a crystalline substance melting at 154° (corr.) and showing $[\alpha]_D$−12.1°. Analysis showed it was another hydrobromide of cholesteryl bromide. Thus it has been found that oxygen exerts an effect on the addition to yield a hydrobromide different from the normal product formed without oxygen, and it is reasonable to assume that the direction of addition is reversed, so that the bromine atom adds to carbon atom 6 and the hydrogen atom to carbon atom 5 (IIIa, IIIb, IIIc, or IIId).

The hydrobromide melting at 154° is more stable than the other melting at 101.5°. It was not changed on boiling in acetone. However, attempts to substitute hydroxyl groups or hydrogen atoms for the both bromine atoms in this hydrobromide failed owing to the ease with which the added molecule of hydrogen bromide was split off under the conditions of the experiments, and nothing but the products from cholesteryl bromide were obtained: On boiling with potassium acetate in acetic acid it was transformed into cholesteryl acetate (Ie). On reduction with sodium and amyl alcohol the hydrobromide again lost hydrogen bromide and gave cholestene (Id). Thus it was impossible to obtain any information of the configuration about carbon atoms 5 and 6.

From the mother liquor of the hydrobromide melting at 154° another crystalline substance was obtained. Its bromine content corresponded to a dibromide of cholesteryl bromide, and on debromination with sodium iodide it gave cholesteryl bromide. As the substance was not obtained in a pure state and melted in a wide range of temperature (84–127°), it could not exactly be determined whether or not it was identical with cholesteryl bromide dibromide (melting point 113°) formed from cholesteryl bromide and bromine.

The formation of the dibromide from cholesteryl bromide by the action of hydrogen bromide and oxygen corresponds to the formation of 1,2,3-tribromopropane and stilbene dibromide from allyl bromide and stilbene respectively by similar treatments.

Experimental.

Materials. Cholesteryl bromide was prepared by the action of phosphorus tribromide on cholesterol in benzene[23] and recrystallized twice from 99% ethanol, melting point 98° (uncorr.). Carbon tetrachloride was prepared by boiling a commercial product with an alkaline solution of potassium permanganate for 7 hours, drying over calcium chloride, and collecting the fraction distilling at 76.5–77°.

The Action of Hydrogen Bromide on Cholesteryl Bromide in Carbon Tetrachloride with the Addition of Catechol. Cholesteryl bromide (10 g.) was dissolved in carbon tetrachloride (30 c.c.), a small amount (0.4 g.) of catechol was added to the solution (catechol remained mostly undissolved), and dry hydrogen bromide was passed into the solution for 8 hours. The solution was washed with water several

(23) R. Kolm, *Monatsh.*, **33** (1912), 447.

times until the washing-water did not give a green colouration with ferric chloride, dried over anhydrous sodium sulphate, and evaporated at the temperature not exceeding 40°, when a yellowish oil remained. It was dissolved in ether (50 c.c.). On adding methanol to the ethereal solution a colourless crystalline precipitate separated out. The process of dissolving in ether and precipitating with methanol was repeated five times. The hydrobromide obtained in this way forms colourless fine needles melting at 101.5° (corr.). Found: Br,30.24. Calculated for $C_{27}H_{46}Br_2$: Br,30.12%. $[\alpha]_D^{26°} = +5.36°$ (11.2 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{26°} = +0.06°$).

The Action of Hydrogen Bromide on Cholesteryl Bromide in the Presence of Ferric Chloride. Hydrogen bromide was passed for 6 hours into a solution of cholesteryl bromide (11 g.) in carbon tetrachloride (60 c.c.) with the addition of ferric chloride hexahydrate (0.2 g.). The dark brown reaction mixture was washed with water to a light yellow solution, which was dried over anhydrous sodium sulphate and evaporated below 30°. The residue was dissolved in ether and precipitated with methanol. This process was repeated three times. Yield 4.5 g. Melting point 101° (corr.). No depression of the melting point in admixture with the above specimen of the hydrobromide.

The Action of Hydrogen Bromide on Cholesteryl Bromide in Ether. When hydrogen bromide was passed for 2 hours into a solution of cholesteryl bromide (10 g.) in ether (75 c.c.), the liquid separated into two layers. The crystals from the upper layer were dissolved in ether and precipitated with ethanol. This process was repeated four times. Yield 1 g. Needles melting at 101.5° (corr.). No depression of the melting point was observed in admixture with the specimen obtained in carbon tetrachloride in the presence of catechol. Found: Br,30.49. Calculated for $C_{27}H_{46}Br_2$: Br,30.12%.

The Action of Hydrogen Bromide and Oxygen on Cholesteryl Bromide in Carbon Tetrachloride. The mixture of hydrogen bromide and oxygen was passed for 3–7 hours into a solution of cholesteryl bromide (10 g.) in carbon tetrachloride (30 c.c.). The solution became first yellow and then wine-red. After diluting with an equal volume of carbon tetrachloride, the solution was washed with water, when it became light brown. The solution was then dried over anhydrous sodium sulphate and evaporated below 30°. The substance remained was dissolved in ether and precipitated with methanol. When the process of dissolving in ether and precipitating with methanol was repeated seven or eight times, the hydrobromide was obtained in colourless needles melting at 154° (corr.). Found: Br,29.65. Calculated for $C_{27}H_{46}Br_2$: Br,30.12%. $[\alpha]_D^{26°} = -12.1°$ (15.7 mg. in 1 c.c. chloroform solution, $l = 1$ dm., $\alpha_D^{26°} = -0.19°$).

The hydrobromide was hardly affected on boiling in acetone for five hours.

On concentrating the mother liquor of the second recrystallization of the above hydrobromide an impure crystalline substance melting in the range of 84–127° (uncorr.) was obtained. It showed a composition of a dibromide of cholesteryl bromide. Found: Br,39.80. Calculated for $C_{27}H_{45}Br_3$: Br,39.34%. The melting point in admixture with the dibromide (melting point 113°, corr.) prepared by adding bromine to cholesteryl bromide was found 90–108° (uncorr.).

The Elimination of Hydrogen Bromide from the Hydrobromide Melting at 101.5°. The hydrobromide melting at 101.5° (0.5 g.) was boiled in pyridine (13–15 c.c.) for 12 hours, and the liquid was poured into water. The precipitated substance was extracted with ether. The ethereal solution was shaken with dilute sulphuric acid and water, dried over anhydrous sodium sulphate, and evaporated. On adding methanol to the oily residue a crystalline substance separated out. It was collected, dissolved in ether, and again precipitated with methanol. The substance thus obtained forms needles melting at 76° (corr.), contains no bromine, and gives a colouration changing through yellow and yellowish brown to red on adding 90% trichloroacetic acid to its chloroform solution. Thus the substance shows the properties of cholestadiene-(3,5).[24]

(24) H. E. Stavely and W. Bergmann, *J. Org. Chem.*, **1** (1936), 567; J. C. Eck, R. L. Van Peursem, and E. W. Hollingsworth, *J. Am. Chem. Soc.*, **61** (1939), 172; I. M. Heilbron and F. S. Spring, *Biochem. J.*, **24** (1930), 133.

The hydrobromide (1 g.) was boiled in acetone (30 c.c.) for 5 hours. The crystalline substance separating out on cooling the acetone solution melted at 97° (corr.) and showed no depression of the melting point in admixture with cholesteryl bromide (mixed melting point 98°,corr.).

The Action of Potassium Acetate on the Hydrobromide Melting at 154°. The hydrobromide melting at 154° (1 g.) was boiled with anhydrous potassium acetate (20 g.) in glacial acetic acid (60 c.c.) for 10 hours. The acetic acid was neutralized with concentrated aqueous potassium hydroxide and the reaction product was extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulphate, and evaporated in vacuum. The acetyl group was determined with the crude product: 0.328 g. of the substance was boiled with 20 c.c. of ca. 0.5 N alcoholic potash for 2 hours and the remaining alkali was titrated with 0.441 N hydrochloric acid, of which 22.68 c.c. was consumed, while in a blank test 20 c.c. of the aloholic potash consumed 24.46 c.c. of the hydrochloric acid. (Found: CH_3CO,10.30. Calculated for cholesteryl acetate, $C_{27}H_{45}OCOCH_3$: CH_3CO,10.04%.

The product of the above saponification was extracted with ether. The substance obtained from the ethereal solution was recrystallized from methanol and identified with cholesterol by the melting point (148°,corr., mixed melting point 148.5°,corr.) and by the formation of the digitonide.

The Reduction of the Hydrobromide Melting at 154° with Sodium and Amyl Alcohol. The hydrobromide melting at 154° was reduced with sodium in amyl alcohol and the product was recrystallized several times from acetone to colourless small needles melting at 90.5–92° (corr.). It gave a yellow colouration with tetranitromethane. It was identified with cholestene: A mixture with an authentic specimen (melting point 90.5–92.5,corr.) melted at 90.5–92° (corr.).

The Debromination of the Dibromide from the Mother Liquor of the Hydrobromide Melting at 154°. The substance (0.2 g.) was dissolved in benzene (10 c.c.) and sodium iodide (2 g.) dissolved in ethanol (15 c.c.) was added. The mixture was heated on the water bath for 2 hours. The solvents were removed in vacuum and the residue was extracted with ether. The ethereal solution was washed with water, dried over anhydrous sodium sulphate, and concentrated. The crystalline substance separating out on adding methanol was identified with cholesteryl bromide: It melted at 97–97.5° (corr.) alone and at 98° (corr.) in admixture with an authentic specimen.

Summary.

Hydrogen bromide was added to cholesteryl bromide in carbon tetrachloride. In the presence of catechol or ferric chloride a hydrobromide melting at 101.5° was obtained. Addition in ethereal solution gave the same product. Simultaneous action of oxygen yielded another hydrobromide melting at 154° and a substance with the composition of a dibromide of cholesteryl bromide. The direction of addition of hydrogen bromide is assumed to follow the examples of additions to simpler ethenoid compounds. The properties and the transformations of the hydrobromides are described. The both hydrobromides lose hydrogen bromide more or less easily.

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On the Nature of Foam. VII.[1] Foam Formation of Mixed Aqueous Solution of Saponin and Ethyl Alcohol.

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(Received September 27, 1940.)

It is a problem of fundamental importance for the study of foam phenomena to clear the mechanism of its formation.

It has already been pointed out that it is reasonable to assume two factors to explain the mechanism of foam formation, namely, the stability of foam and foam producing power[2]. Though we cannot yet at present define these two quantities satisfactorily, they are briefly explained as follows. In ordinary cases, the stability of foam has relatively close relationship to a life of foam, for example, an aqueous solution of saponin or soap gives fairly stable foam on shaking which sometimes shows a life of several days, while in the case of solutions of alcohols or fatty acids, foam is unstable and short-living which last for only about thirty seconds. Foam is stabilized chiefly by the existence of plasticity or rigidity in foam film[3], of saponin for example. Foam producing power, on the other hand, means the degree of easiness with which foam is produced. This factor is rather pronounced in solutions of alcohols and fatty acids. In practice, measurements carried out in properly dilute solutions of alcohol (butyl alcohol for example) and saponin shows that the foam volume[4] of the former is larger although its life is shorter than those of the latter. Foam producing power is favoured by low surface tension and perhaps low viscosity, as in the case of aqueous solutions of surface active substances.

Now, there occurs a case where a considerable degree of foam formation is observed in dilute mixed solution of saponin and ethyl alcohol, even when foam cannot be produced in solutions which contain these solutes separately but in the same concentrations as in the mixed solution. Such a foam formation of mixed solution can be explained as the results of combined effects of stability due to saponin and foam producing power due to ethyl alcohol, either of which alone is not sufficient for the foam formation as in the cases of separate solutions.

Present paper describes the results and explanations of these and some other related phenomena.

Apparatus and Measurement. Measurements of the degree of foam formation were carried out with such mixed aqueous solutions of saponin

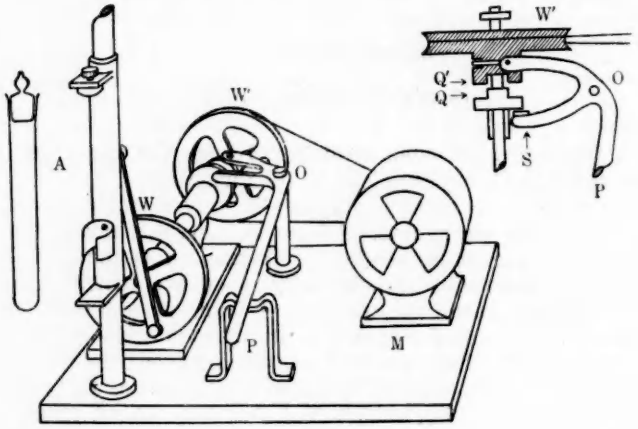
(1) The former reports are the followings: Sasaki, this Bulletin, **11** (1936), 797; **13**(1938), 517; **13**(1938), 669; **14**(1939), 3; **14**(1939), 63; **14**(1939), 107; **14** (1939), 250.

(2) Sasaki, this Bulletin, **13** (1938), 517.

(3) Wilson and Ries, Colloid Symposium Monograph, **1** (1923), 145; Talmud, Suchowolskaja and Lubman, *Z. physik. Chem.*, A **151** (1930), 401.

(4) Volume of foam measured immediately after the stop of shaking is relatively in close relation to foam producing power.

and ethyl alcohol as they contain both solutes in a constant and varying concentration respectively.



P —handle, rotatable around the point O.
W —wheel with a crank.
W′—wheel, connected to P and be able to slide on axis of W.
S —brake acting on W.
M —induction motor.
A —test tube and its supporter.
Q, Q′—projections belonging to W and W′ respectively and acting as joint between them.

Fig. 1.

Foam was produced by shaking apparatus as shown in Fig. 1. In this Figure, by moving handle P rightwards, wheel W′ shifts towards W to which it is connected by means of joint Q and Q′. Then, the test tube A containing liquid is made to vibrate by setting the motor M in motion. The vibration is interrupted by leftward movement of the handle P with resulting action of brake S upon W.

Conditions of measurement were the same as in the former report[5], namely, 10 c.c. of solution for measurement is introduced in a well stoppered test tube (1.5 cm. in diameter and 15 cm. in length) and is shaken 50 times for 10 seconds with an amplitude of 12 cm. After shaking, following quantities are measured.

H_0, height of foam zone (in cm.) produced immediately after the stop of shaking.
H_5, height of foam zone in five minutes after shaking, in the case required.
L , Life of foam (in second).

(5) Sasaki this Bulletin, **13** (1938), 669.

Results of Measurement. The results of measurement were shown in Tables 1, 2 and Figs. 2–5. Concentration of saponin was in one case 0.009085 g./l. as in Table 1, Fig. 2 and Fig. 3, (system A) while in another case, it was 0.001820 g./l. as in Table 2, Fig. 4 and Fig. 5. (system B). These conditions were adopted as the critical concentration, namely, the former concentration of saponin in water corresponds to the heighest possible dilution at which solution still foams, while at latter concentration, aqueous solution of saponin foams no more. In Figs. 2–5, H_0, H_5 and L are quantities referring to the mixed solution, and H_0' and L' are those referring to the solution of alcohol without saponin, for comparison.

Table 1.

Conc. of saponin (g./l.)	Conc. of alcohol (mol/l.)	H_0 (cm.)	H_5 (cm.)	L
0.009085	0	0.8	0	65.5 sec.
0.009085	0.0005143	0.7	0	25.5 sec.
0.009085	0.002572	0.8	0.5	>5 min.
0.009085	0.005143	1.2	0.8	>5 min.
0.009085	0.02571	2.3	1.7	>5 min.
0.009085	0.05143	3.1	2.2	>5 min.
0.009085	0.2571	4.8	3.4	ca. 2 hour
0.009085	0.5143	4.7	3.5	>5 min.
0.009085	0.7713	3.9	1.3	>5 min.
0.009085	1.029	4.4	0	17.6 sec.
0 009085	1.543	4.6	0	10.0 sec.
0.009085	17.13	0	0	0 sec.

Table 2.

Conc. of saponin (g./l.)	Conc. of alcohol (mol/l.)	H_0 (cm.)	L (sec.)	H_0' (cm.)	L' (sec.)
0.001820	0	0	0	0	0
0.001820	0.0005143	0.5	0	0	0
0.001820	0.002572	0.6	11.8	0	0
0.001820	0.005143	0.8	54.3	ca. 0.5	0
0.001820	0.02571	1.4	57.0	1	2.0
0.001820	0.05143	2.0	86.0	1.2	5.0
0.001820	0.2571	3.4	59.0	1.9	7.8
—	0.5143	—	—	1.8	7.6
0.001820	0.7714	3.2	12.0	—	—
—	1.029	—	—	3.1	7.5
0.001820	1.543	2.7	5.5	2.7	7.1
—	5.143	—	—	1.7	2
0.001820	17.13	0	0	0	0

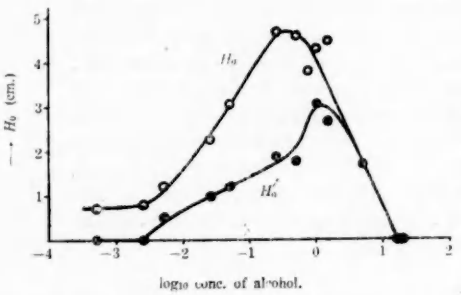


Fig. 2. Mixed solution of saponin and alcohol. saponin = 0.009085 g./l

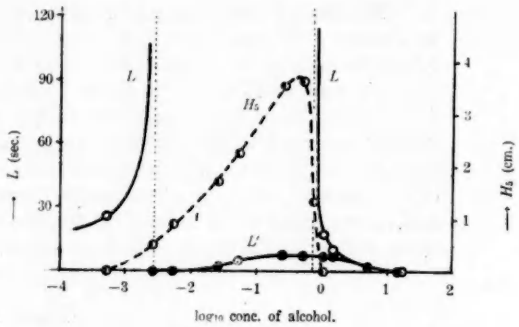


Fig. 3. Mixed solution of saponin and alcohol. saponin = 0.009085 g./l.

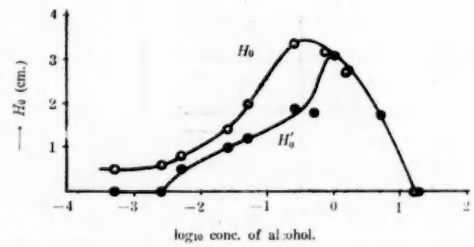


Fig. 4. Mixed solution of saponin and alcohol. saponin = 0.001820 g./l.

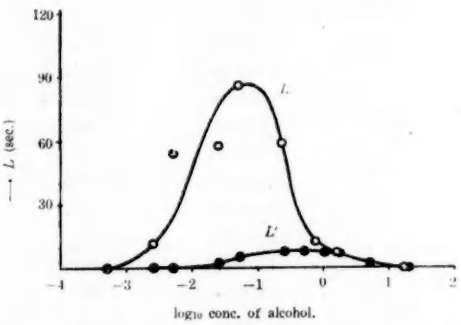


Fig. 5. Mixed solution of saponin and alcohol. saponin = 0.001820 g./l.

It can be seen in Figs. 2 and 4, that diagrams of $H_0 \sim$ conc. and $H_0' \sim$ conc. as a whole are analogous to each other. The foam height of mixed solution shows a magnitude which can be expected from that of corresponding alcohol solution, that is, the foam height of mixed solution is mainly determined by alcohol, and saponin shows only a little or no effect at all. When we observe, however, the relation between life of foam and concentration of alcohol in mixed solution as shown in Figs. 3 and 5, we find the followings. In the system A, foam life of saponin solution is increased in length from 65 seconds to more than 5 minutes by the addition of merely about 0.0026 mol/l. of alcohol. In the optimum case, foam lasting for about two hours can be obtained by the addition of 0.2571 mol/l. of alcohol. Foam life of solution containing alcohol alone, is also very small compared with that of mixed solutions as shown in Fig. 3. When foam life amounts to more than five minutes, the result of its measurement becomes uncertain. In such a case, foam height in five minutes after shaking is indicated instead of its life, for convenience. Foam life of the mixed solution is remarkably reduced by the addition of alcohol in excess (over concentration of 0.77 mol/l.). In the system B, the phenomena are

similar, though not so marked as in the system A. In this system, a mixed solution containing both 0.001820 g./l. of saponin and 0.005143 mol/l. of alcohol shows a foam life of 54 seconds, while solutions containing these amounts of solutes separately do not foam at all. ($L=0$). As a whole, foam life of saponin solution is fairly increased in length by the addition of alcohol within the region of concentration covering over from 0.0026 mol/l. to 0.77 mol/l. for both systems.

Discussion. Now, the explanation of the above phenomena is attempted.

(1) On the stand point of foam formation, saponin solution is marked for its stabilizing action, while foam producing power is characteristic for alcohol solution as described in the introduction of this paper. It is, therefore, reasonable to assume that the foam height of mixed solution which is perhaps closely related to foam producing power, is mainly determined by the properties of alcohol, and is not affected by the presence of saponin, because of its little foam producing power in such a dilution as in the present experiment. The remarkable increase in length of foam life of mixed solution, on the other hand, can be explained either as the stabilizing action of saponin for the foam formation of alcohol solution, or inversely, as the foam producing action of alcohol for saponin solution, that is, the action of alcohol to increase the degree of dispersion of saponin foam. Thus, the life of foam measured under these conditions is considered to be affected both by the foam producing and stabilizing action of solutes. In the region of such remarkable foam formation of the mixed solution, these two actions are attributed to saponin and alcohol respectively.

(2) In the region of mixed solutions, however, where the concentration of alcohol exceeds certain limit[6], above two actions are exclusively determined by alcohol. This is especially pronounced in the case of the system B as shown in Figs. 4 and 5. Here, the life and height of foam measured in a mixed solution containing alcohol in concentration of more than 1.029 mol/l, shows the same value as in the corresponding alcohol solution without saponin. In such a case, properties of liquid films consisting foam are considered to be the same for both solutions, practically. The similar phenomena can also be observed in the system A, though a little less pronounced. These may be explained either from the preferential adsorption of alcohol in surface of foam film with an exclusion of sapoin, or from dehydrating action of alcohol for saponin particles in foam film. Concerning to the former explanation, the possibility may be suggested for observing a state of preferential adsorption of a solute from a mixed solution by the measurement of properties exhibited by liquid films, such as the life and height of foam. As to the latter explanation, it is interesting, in this connection, to describe further the properties of foam as a disperse system.

(3) As a disperse system, foam can be considered to be a suspension or emulsion, the disperse phase of which is replaced by air or by the other gases, and so it is a kind of hydrosol in wider sence. Foam can, therefore, be divided also into two types, that is, hydrophilic and hydro-

(6) 1.543 mol/l. and 1.029 mol/l. for systems A and B respectively.

pholic foams[7], quite analogous to the hydrophilic and hydrophobic sols in the case of aqueous suspension[8]. Hydrophilic foam is relatively stable as produced in saponin or soap solution, and is insensitive for electrolyte. Hydrophobic foam, on the other hand, is unstable like that of alcohol or fatty acid solution, and is sensitive for electrolyte. Hydrophilic foam can also be rendered unstable by the addition of alcohol with resulting dehydration of foam film, just as in the case of hydrophilic sol. This is the case described in (2). But, just reverse to this phenomenon, we have also noticed the increase in length of the life of saponin foam by the addition of relatively small amount of alcohol as shown in the preceding section. We cannot, however, find the similar instance in aqueous suspension at all. This lack of analogy between foam and suspension is explained as follows.

In the case of aqueous suspension, effects of alcohol are measured in a system already dispersed preceding to the addition of alcohol, while in the case of foam, the same effects are observed in a system which is dispersed by shaking or by other means after the addition of alcohol. Therefore, in latter case, effects of alcohol during the process of dispersion and consequently upon the foam produced, must be considered in addition to those in the case of aqueous suspension. Accordingly, the phenomena can be explained if we take into account of the fact that the decrease in surface tension of saponin solution and some other effects which are produced by the addition of alcohol, favour a high degree of dispersion[9].

The author wishes to express his hearty thanks to Nippon Gakuzyutu Sinkokwai (Japan Society for the Promotion of Scientific Research) for a grant.

Summary.

(1) The foam formation of mixed aqueous solution containing saponin in a constant amount and ethyl alcohol in varying concentration was studied. Life of the foam produced in aqueous solutions of saponin (concentrations being 0.009085 g./l. and 0.001820 g./l.) is remarkably increased in length by the addition of alcohol within the region of concentration covering over from 0.0026 mol/l. to 0.77 mol/l. Addition of alcohol in concentration exceeding 0.77 mol/l. again renders the foam unstable.

(2) Attempts were made to explain the mechanism of foam formation relating to the above phenomena.

(3) Foam and hydrosol were compared with respect to their properties as a disperse system, from which some resemblances as well as differences were pointed out between them.

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(7) The terms, "lyophile Schäume" and "lyophobe Schäume" were also introduced by Bartsch; see the footnote (8).

(8) Bartsch, *Kolloidchem.* Beihefte, **20** (1925), 1.

(9) In the case of emulsion, however, alcohol shows the effect similar to the case of this foam system. In such a case, alcohol is sometimes called "introfier"; see also, Holms, "Laboratory Manual of Colloid Chemistry", 3rd ed., 167, New York (1932).